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The Rate of Oxidation of Linseed Oil

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The Rate of Oxidation of Linseed Oil

A DISSERTATION

PRESENTED TO THE

FACULTY OF PRINCETON UNIVERSITY

IN CANDIDACY FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

BY

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Accepted by the Department of Chemistry

June 1924

THE RATE OF OXIDATION OF LINSEED OIL*

BY WILLIAM ROGERS, JR.

Considering the technical importance of the drying of oils, it is surprising that accurate quantitative study of their rates of oxidation has only recently been made. The early experiments were undertaken in order to fix the composition of linseed oil from a study of the oxidation products. Although Cloez[1] observed and studied the volatile products of oxidation; he used the increase in weight of a linseed oil film as a measure of the rate of oxidation. He showed the accelerating effect of different coloured light, technical driers, and partially oxidized oil on this rate. Plotting the change in weight against time, he obtained curves which developed slowly, rose steeply to a maximum, and then fell back to a level of constant weight. Coffey[2] points out that Mulder in 1867 recognized the formation of volatile products of oxidation in this reaction. Yet subsequent workers neglected to allow for the effect of their formation when determining the amount of oxygen taken up by the oil.

Bauer and Hazura[3] allowed a film of oil, containing lead oxide, to dry on glass plates and then analyzed the film. This is permissible in a study of the solid products of oxidation, and is adaptable to a qualitative estimation of the composition of the original oil, but a quantitative statement concerning this composition is hardly possible by this method.

In order to obtain a method for comparing the rates of drying of variously treated oils and the efficiency of commercial driers, Kissling[4] showed the reaction was purely chemical and independent of bacteria, and used the increase in weight of a film of the oil to indicate the rate of oxidation. His data showed the formation of volatile products. He was aware of this fact[5] but was satisfied that his test gave comparable results[6]. Using the time required by an oil film to dry as the criterion for the rate of oxidation, the dryness was determined by touching the film, Amsel[7] offers a method for detecting the presence of adulterants in linseed oil. In a subsequent paper[8] he used this method to study the drying efficiencies of different driers. That such methods would lead to unsatisfactory results was inevitable. The controversy which followed between Kissling[9], Amsel,[10] Lippert,[11] and Weger[12] is a testimony to the inaccuracy of their methods.

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* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Compt. rend., **61**, 236, 321, 981 (1865).

[2] J. Chem. Soc., **119**, 1152 (1921).

[3] Z. angew. Chem., **1**, 455 (1888).

[4] Z. angew. Chem., **4**, 395 (1891).

[5] Z. angew. Chem., **8**, 44 (1895).

[6] Z. angew. Chem., **11**, 361 (1898).

[7] Z. angew. Chem., **8**, 73 (1895).

[8] Z. angew. Chem., **8**, 262 (1895).

[9] Z. angew. Chem., **4**, 395 (1891); **8**, 44 (1895); **11**, 361, 613 (1898).

[10] Z. angew. Chem., **9**, 429 (1896); **10**, 303, 344, 369 (1897).

[11] Z. angew. Chem., **10**, 306 (1897); **11**, 412 (1898); **13**, 133 (1900); **16**, 365 (1903).

[12] Z. angew. Chem., **9**, 531 (1896); **10**, 401, 542, 560 (1897); **11**, 490, 507, 614 (1898); J. Soc. Chem. Ind., **17**, 257, 360 (1898).

Weger showed the wide discrepancy between Kissling's results which used the time at which the film attained maximum weight as the criterion for dryness, and his own results which relied on the actual hardening of the film. This he attributed to the fact that maximum weight did not necessarily coincide with the point at which the film dried; and also showed that four factors, (a) Variation in temperature, (b) Variation of light intensity, (c) Changes in humidity, (d) Variability in the air currents, produce great differences in the time using either method. He came to the conclusion that only those results obtained by running the reactions simultaneously and side by side were comparable. This is true qualitatively but for any knowledge of the process a controllable and quantitative method for studying the oxidation is necessary. The discussion brought out two interesting points, (a) metallic driers must be soluble in the oil to give accelerated drying,[1] (b) The above variables must be controlled to give comparable results.

With these facts in mind, Genthe[2] devised a method which did give reproducible results and marked the first determination of the true rate of oxidation. He supported the oil on filter paper which eliminated the effects due to a thick film, and suspended this paper in a flask closed by a ground-glass stopper through which a manometer tube passed. Solid potassium hydroxide served to absorb the moisture in the flask and also to absorb the volatile products of oxidation. Thus he could always duplicate the temperature by immersing the flask in a thermostat, shut out the light by use of brown glass vessels, and eliminate the effect of moisture. The advisability of these precautions is shown by the reproducibility of his results. This offers a course of procedure which gives chemically significant and comparable results.

He noted that it was necessary to clean his pipettes and vessels with cleaning solution after each run in order to duplicate his results. This is an indication of the effect of small concentrations of catalyst; and is borne out by our results which show marked acceleration with only 0.0003 per cent of cobalt as cobalt linoleate to catalyse the reaction. The percentage is calculated as percentage of metal. With Uviol glass vessels he found that the ultra-violet light from a mercury vapour lamp caused the same degree of oxidation in one day which the dark reaction reached in fifty-five days. Weger (loc. cit.) had previously shown that direct sunlight gave a hard film, using manganese salts as driers, in one half the time required in diffused light. One very important observation is shown from his curves which represent the reactions using air and pure oxygen, i. e. raising the oxygen pressure from 150 mm. to 760 mm. The raw linseed oil is oxidized at only a slightly greater rate in pure oxygen at room temperature than in air, while the catalysed reaction is not accelerated at all by the use of pure oxygen. At 95° C pure oxygen does not alter the rate until the upper flat portion of the curve is reached. The effect, as shown by his curves, of oxidizing the oil with no potassium hydroxide in the flask to absorb the volatile products is very instructive and indicates why results from

[1] Loesner also arrives at this conclusion, J. Soc. Chem. Ind., **17**, 608 (1898).

[2] Z. angew. Chem., **19**, 2087 (1906).

methods which neglect this factor can have little or no value. His results are expressed in manometer readings from each determination and are thus a function of the particular size of vessel used. He does state, however, that his final results correspond to about 26 per cent of oxygen absorbed, 34.7 per cent in the case of pure oxygen at 95° C.

Those of Fahrion's results[1] which are based on conclusions depending on the increase in weight of a film of oil as a measure of the oxidation are not very conclusive. The same applies to Fokin's results.[2]

Genthe's work apparently made little impression. Sabin,[3] who had tried to measure the volatile products of oxidation, used the change in weight of a film to show the rate of oxidation. He duplicated the observations of Cloez (loc. cit.) on the shape of the curves obtained by plotting this change against time. This phenomenon is also disclosed on analyzing Kissling's data.

In an attempt to show a relation between the iodine number of the oil and the total percentage of oxygen it will absorb, Ingle[4] also uses the increase in weight of an oil film to indicate the amount of oxygen taken up. He also observed that the weight decreases after the maximum is reached, a direct evidence of volatile products of oxidation, yet neglected them in his value for the final percentage of oxygen taken up. This renders his explanation of the mechanism of the reaction, which is based on this value, of doubtful significance. He later used the time required for the oil supported on cotton wool to reach 200° C in his tester as a characteristic property,[5] and compares the relative efficiency of different metallic soaps in this respect.

Comparison of the rate of oxidation of linseed, soya-bean, china-wood, and fish oils is given by Rodman, Weith, and Brock[6] using the change of weight in films of the oils as a measure of this rate.

Baly[7] shows the absence of lead in the vapours from paints and shows the presence of unsaturated aldehydes. Gardner[8] arrives at the same conclusion as Baly and also detects the presence of carbon monoxide in the vapours. He states that the character of a pigment affects the nature of the volatile products. However, Klein[9] has questioned the validity of this result and indicates that the amount of carbon monoxide found by Gardner can be accounted for by the action of the sulphuric acid used in the absorption system on the formic acid in the vapours. But King[10], taking the precautions suggested by Klein, found carbon monoxide present.

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[1] Z. angew. Chem., **4**, 540 (1891); **5**, 171 (1892); **23** I, 722 (1910); Chem Ztg., **28**, 1196 (1904).

[2] Z. angew. Chem., **22** II, 1451 (1909).

[3] J. Soc. Chem. Ind., **25**, 579 (1906); J. Ind. Eng. Chem., **3**, 84 (1911).

[4] J. Soc. Chem. Ind., **32**, 639 (1913).

[5] J. Soc. Chem. Ind., **35**, 454 (1916); **36**, 317 (1917).

[6] J. Ind. Eng. Chem., **5**, 630 (1913).

[7] J. Soc. Chem. Ind., **31**, 515 (1912).

[8] J. Ind. Eng. Chem., **6**, 91 (1914).

[9] J. Ind. Eng. Chem., **7**, 99 (1915).

[10] J. Ind. Eng. Chem., **7**, 502 (1915).

Wise and Duncan[1] show the effect of various metallic soaps on the rate of change in weight of oil films, and by a close control of conditions obtain smooth curves. The significance of the maxima in these curves is explained by Friend.[2] They represent an equilibrium between amounts of oxygen taken up and the loss of volatile products. Any condition altering the loss will alter this maximum. This would make all the previous figures for the total percentage of oxygen absorbed much too low, the difference between them and the true value being roughly the percentage of volatile products formed. The values range from 15 to 20 per cent, the usual figure obtained is 18 per cent. Olsen and Ratner[3] supported linseed oil on glass wool and passed dry, carbon dioxide free, air over it for a period of 74 days. The volatile products were absorbed from the air coming from the flask containing the oil. The oil increased in weight by 18.05 per cent, 14.51 per cent of water was formed, and 5.21 per cent of carbon dioxide and organic matter was given off, thus giving a total of 37.80 per cent for the final amount of oxygen absorbed.

Coffey[4] credits Friend (Proc. Paint and Varnish Soc. May, 1914) with the first true oxygen absorption curves. It would seem that Genthe (loc. cit.) has the prior claim. In his calculations he assumes that the rate of oxidation is dependent on the oxygen pressure. However, Genthe has shown that this is not the case at 95° C and over the time used by Coffey. His curves are thus too steep and would have been more nearly correct had he neglected to correct for the variation in oxygen pressure during the reaction. Recently Rhodes and van Wirt[5] have raised the figure for final oxygen absorption, which Coffey placed at 28 per cent, to 36 per cent. The higher value is supported by Olsen and Ratner (loc. cit.) and by Genthe using pure oxygen at 95° C. Had Coffey extended his observations over a greater period of time he would have undoubtedly arrived at a higher figure. Our experiments have shown that even when 36 per cent of oxygen has been absorbed oxidation is still occurring though slowly. In light the oxidation is faster and may be continued until the whole film is oxidized.

In a later paper, Coffey[6] attempts to prove that driers are not catalysts. He observed that when he dusted the surface of the oil with drier his values for final oxygen absorption were lowered, thus showing that they change the course of the reaction. He is not sustained in this by Rhodes and van Wirt nor by Genthe. The result is probably due to his method of dusting the surface of the oil with the drier, thus covering the surface; and, as Weger has pointed out, a drier must be intimately mixed if not in solution with the oil to be effective. Consequently his deduction that driers are not catalysts is erroneous.

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[1] J. Ind. Eng. Chem., **7**, 202 (1915).
[2] J. Chem. Soc., **111**, 164 (1917).
[3] J. Soc. Chem. Ind., **31**, 937 (1912).
[4] J. Chem. Soc., **119**, 1152, 1408 (1921).
[5] J. Ind. Eng. Chem., **15**, 1125 (1923).
[6] J. Chem. Soc., **121**, 17 (1922).

His method of dusting probably produced metallic soaps and hydrolysed products of different oxidation capacities.

The above résumé of the literature concerning the rate of oxidation of linseed oil is given to show the difficulties in approaching a problem of this sort. Most of the data are confusing and often contradictory. Statements to the effect that sunlight cuts the drying time in half are not very enlightening unless we have a definite criterion for dryness and know the intensity of the light falling on the oil. Comparison of the relative efficiency of driers as well as different concentrations of the same drier are not reliable unless we have a reproducible method for the study of the reaction. It is felt by us that the method originally proposed by Genthe, and used with practical modifications by Coffey and Rhodes and van Wirt, offers such a possibility.

The action of inhibitors on different autoxidizable organic compounds such as styrolene, aldehydes, and acrolein has been studied by Moureu and Dufraisse.[1] The inhibitors in general are compounds of the phenol type such as naphthol, hydroquinone, pyrogallol, and the like. Their conclusions are, that inhibitors are true negative catalysts, that they remain unchanged at the end of the reaction, and in no way alter the total amount of oxygen absorbed. They only reduce the rate of the reaction. They found that a film of linseed oil containing an inhibitor remained in the fluid state for three years.

This research was undertaken to give a convenient method for determining the rate of oxidation of non-volatile oils at different temperatures, to study the effect of varying the concentration of drier on the rate of oxidation of linseed oil, to note the action of inhibitors on the catalysed and normal reactions, to show the effect of temperature on these reactions, and to give a quantitative statement on the effect of light on the reaction.

Experimental Part

The apparatus used was essentially that proposed by Genthe, with practical modifications suggested by experimental difficulties met in an earlier investigation. It consisted of a vessel of the gas-wash-bottle type, about 200 cc. in volume. It was fitted with a mercury sealed ground glass stopper, having inlet and outlet tubes of the usual form. A vacuum-tight stop-cock was sealed to the inlet tube, a manometer to the outlet tube. For use at 100° C. the vessel was made in test tube form.

The oil was made up in solutions of the same strength, so that one cubic centimeter of solution contained 0.200 g. of oil. The drier was added as an 8 per cent solution of cobalt linoleate in turpentine. The required amount of drier or inhibitor was weighed in a 50 cc. volumetric flask, 10 g. of oil were then weighed in the flask, and the contents diluted to the mark with absolute ether or ligroine (B.P. 50°-60°). A piece of filter paper, 15 cm. x 6 cm., folded to go in the vessel readily absorbs one cubic centimeter of such solutions. The bottom of the vessel was covered with a layer of grains of potassium hydroxide and covered with glass wool. The solvent was partially evaporated before placing the paper in the reaction vessel The oiled paper

[1] Compt. rend., **174,** 258; **175,** (1922); **176,** 624, 797 (1923).

was put in place, the stopper fitted and sealed with mercury, and a current of dry carbon dioxide free air blown through the apparatus for five minutes. It was then placed in the thermostat, a rapid current of air passed through for one minute, and one minute allowed for filling the manometer. The stopcock was closed and readings made at regular intervals. When the dimunition in pressure reached 100 mm. the oxygen was replenished from a burette at known conditions of temperature and pressure. This volume of oxygen gave a calibration for the apparatus. From this calibration the manometer readings were transformed to percentage of oxygen taken up, expressed in terms of per cent by weight of oil.

Coffey (loc. cit.) has drawn attention to the futility of making equations with any physical significance fit the oxidation curves of such a complex mixture as linseed oil. Consequently it has been deemed best to use the curves themselves as the medium for showing our results.

The following is a typical set of data for the curves.

TABLE I

Rate of oxidation of linseed oil with 0.003% Co at 40° C.

Time in min.	Manometer readings in mm.	Atmospheric pressure.	Corrected manometer readings.	Percentage of oxygen absorbed.
0	0.0	750	0.0	0.00
23	0.0	750	0.0	0.00
30	−1.0	750	−1.0	0.19
40	−2.0	750	−2.0	0.37
60	−6.0	750	−6.0	1.11
80	−12.0	750	−12.0	2.22
100	−19.5	750	−19.5	3.61
120	−27.5	750	−27.5	5.10
140	−37.0	750	−37.0	6.86
160	−46.0	750	−46.0	8.53
180	−54.0	750	−54.0	10.00
200	−62.0	750	−62.0	11.11
220	−69.0	750	−69.0	12.80
240	−75.0	750	−75.0	13.90
280	−84.5	751	−83.5	15.65
380	−100.0	754	−96.0	17.77
	0.0			
410	−2.0	754	−98.0	18.15
580	−17.0	757	−110.0	20.40
600	−18.0	757	−111.0	20.59
1120	−44.0	760	−134.0	24.80
1520	−64.0	763	−151.0	28.00
2660	−74.5	767	−157.5	29.40

When the manometer read 100 mm., after 380 min., the oxygen was replenished from a burette; 28.40 cc. of oxygen at 24°.0 C. and 754 mm. were required. This was equivalent to 25.91 cc. at standard conditions, and from

the following calculation, $25.91 \times 96/100 = 24.88$, the amount of oxygen actually absorbed is obtained. This corresponded to 17.77 per cent of oxygen. From this value, the value of each division on the manometer scale can be determined and the readings transformed to percentage of oxygen absorbed. The percentages so obtained are plotted against time, and the curves drawn through these points represent the rate of oxidation of the oil.

Discussion of Results

The effect of the temperature on the rate of oxidation of raw linseed oil is shown in Fig. 1. The increase in temperature has shortened but not

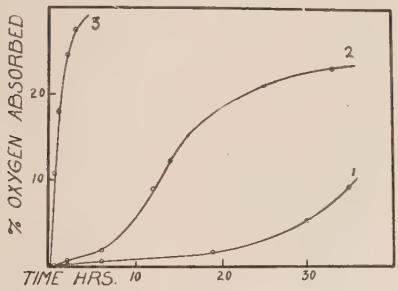

FIG. 1
Linseed Oil
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

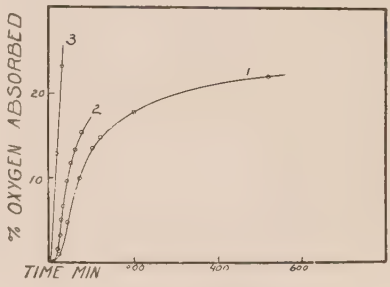

FIG. 2
Linseed Oil with 0.03% Co.
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

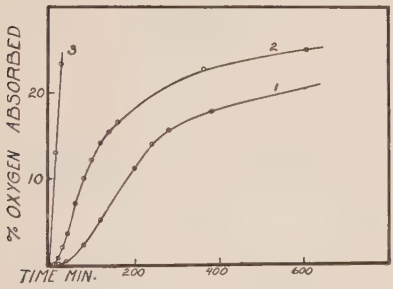

FIG. 3
Linseed Oil with 0.003% Co.
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

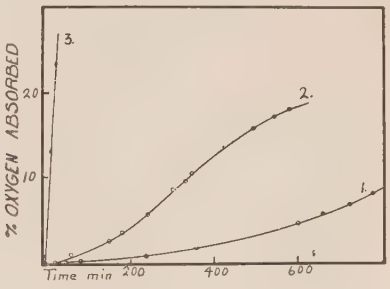

FIG. 4
Linseed Oil with 0.0003% Co.
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

eliminated the induction period. This is not apparent in the curve representing the reaction at 100° due to the large units employed as abscissae but will be shown later.

Cobalt linoleate used as a catalyst does not eliminate this induction period as shown in Figs. 2, 3, and 4. The catalyst was used in three different concentrations corresponding to 0.0003%, 0.003%, and 0.03% of cobalt. These Figs. show the effect of increasing the concentration of the catalyst and increasing the temperature. From Figs. 2 and 3 it is interesting to note that

at 40°, 0.03% of cobalt gives approximately the same rate of oxidation, up to 16% of oxygen absorbed, as 0.003% of cobalt at 50°. Over this part of the curve an increase of ten degrees in temperature is equal to a ten-fold increase in drier.

As the concentration of the drier is increased the effect of increasing temperature is less marked. For instance, the increase in the rate of oxidation indicated in curve 2, Fig. 2 over that of curve 1, Fig. 2 is not as great as the increase of curve 2, Fig. 3 over that of curve 1, Fig. 3. In other words, using 0.03% of cobalt there is not as great an increase in the rate of oxidation at

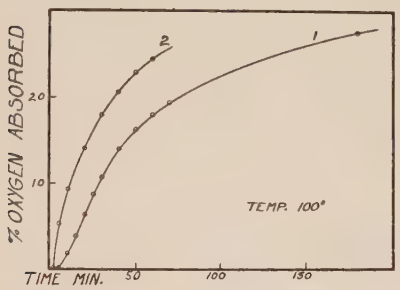

Fig. 5

Curve 1 Linseed Oil

Curve 2 { Linseed Oil with 0.003% Co.
Linseed Oil with 0.003% Co.
Linseed Oil with 0.03% Co.

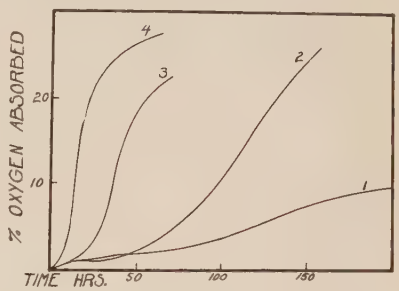

Fig. 6

Curve 1 Linseed Oil + 1% Hydroquinone at 40°

Curve 2 Linseed Oil + 1% Hydroquinone at 50°

Curve 3 Linseed Oil at 40°

Curve 4 Linseed Oil at 50°

50° over that at 40° as in the case of 0.003% of cobalt over the same temperature range. The same applies to curves 1 and 2, Fig. 4 compared with curves 1 and 2 in Fig. 3. A temperature rise from 40° to 50° gives a greater increase in reaction rate using 0.0003% of cobalt than using 0.003% of cobalt.

As the concentration of the catalyst is increased, the induction period is shortened but never eliminated. The general shape of the curve is also not affected. These facts support the theory that the driers act as catalysts for the formation of the auto-catalytic substances formed during the reaction.

Furthermore, at any definite temperature, as the catalyst concentration is increased, the rate of oxidation approaches a maximum value. This indicates that the effect of successive increments in the concentration of the drier is not directly proportional to this increase; and at any temperature a point will be reached beyond which the increase will not further accelerate the rate of oxidation. A startling demonstration of this is shown in curve 2, Fig. 5 which represents the rate of oxidation of the catalysed reaction, using the three different concentrations indicated, at 100°. It means that an hundred-fold increase in the concentration of the catalyst produces no further acceleration in the rate of reaction. Weger (loc. cit.) has already shown that an increase of 0.04% to 0.84% of manganese as manganese resinate, and an increase of 0.1 to 0.7 per cent of manganese as manganese linoleate did not appreciably affect the time required for a linseed oil film to harden at room temperature

Much credence cannot be attached, however, to results determined from the touching method. But these curves show the truth of Weger's deduction that increasing the concentration of drier beyond a certain value will not further accelerate the rate of oxidation.

An attempt was made to study the effect of inhibitors on the normal and catalysed rates of reaction. Hydroquinone was first tried. The results with

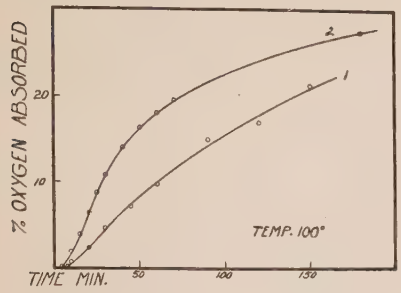

FIG. 7

Curve 1 Linseed Oil + 1% Hydroquinone

Curve 2 Linseed Oil

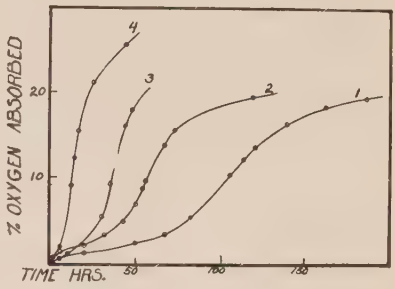

FIG. 8

Curve 1 Linseed Oil+1% β- Naphthol at 40°

Curve 2 Linseed Oil+1% β- Naphthol at 50°.

Curve 3 Linseed Oil at 40°

Curve 4 Linseed Oil at 50°

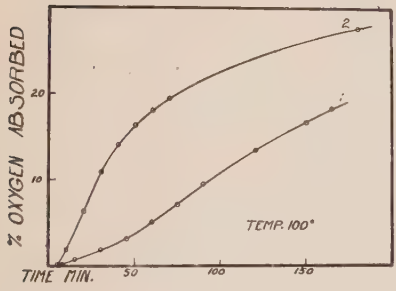

FIG. 9

Curve 1 Linseed Oil+1% β- Naphthol.

Curve 2 Linseed Oil.

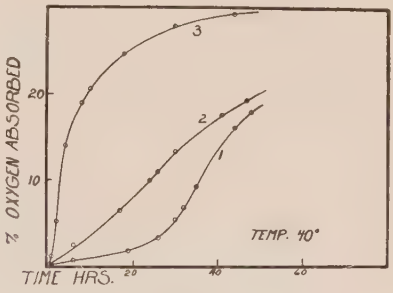

FIG. 10

Curve 1 Linseed Oil Diphenylamine.

Curve 2 Linseed Oil+0.003% Co.+1%.

Curve 3 Linseed Oil+0.003% Co.

this inhibitor were very unsatisfactory. The curves could not be dulpicated within the range of accuracy desired. Fig. 6 shows the average result of the runs at 40° and 50°. Curve 1 Fig. 7 is the average result of ten runs. They do show the trend of the results with inhibitors. This variability may be attributed to the insolubility of hydroquinone in the oil. The heterogeneity of distribution resulting from the separation when the solvent was evaporated would cause the different results. To test this idea 5 mg. of hydroquinone were shaken with 5 cc. of linseed oil at 40° and did not dissolve.

Diphenylamine and beta-naphthol were found to be quite soluble in the oil and gave reproducible results. Figs. 8 and 9 represent the results with linseed oil containing one per cent of beta-naphthol at 40°, 50°, and 100°.

Figure 8 shows the effect of temperature on the rate of the inhibited reaction. The effect of one per cent of diphenylamine present at 40°, 50°, and 100° on the normal and catalysed reaction is shown in Figs. 10, 11, and 12. From a close study of the early stages of the absorption, there is evidence of a rapid reaction which ends quickly. The inhibitors seem to have little effect on this, consequently it is shown very clearly in their curves. Those showing the oxidation rate of raw linseed oil show this reaction also, but it is obscured at 100° and in the presence of catalysts. It points to the presence of a small amount of very readily oxidisable substances or to the absorption of oxygen

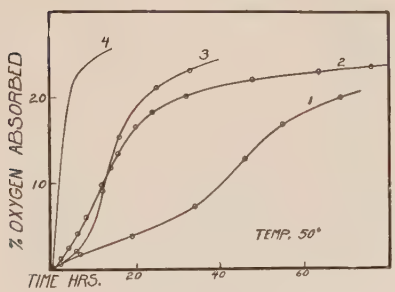

FIG. 11

Curve 1 Linseed Oil+1% Diphenylamine.
Curve 2 Linseed Oil+1% Diphenylamine+0.003% Co.
Curve 3 Linseed Oil.
Curve 4 Linseed Oil+0.003% Co.

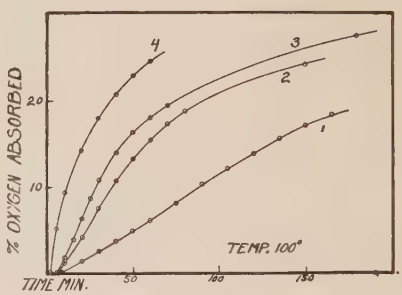

FIG. 12

Curve 1 Linseed Oil+1% Diphenylamine.
Curve 2 Linseed Oil+1% Diphenylamine+0.003% Co.
Curve 3 Linseed Oil.
Curve 4 Linseed Oil+0.003% Co.

more rapidly than the oxidation. The latter explanation is open to serious objection on the ground that the oil film has been in contact with the air for ten minutes before being placed in the thermostat, and in Fig. 8, curves 1 and 2 as well as Fig. 11, curve 1, the three cases in which it is most evident, there is a period of about thirty minutes before the reaction starts. Thus the film has been in contact with the air for forty minutes.

It seems unlikely that the film would remain quiescent for this period and then suddenly saturate itself, which would be the case were this mechanical absorption. Furthermore we would have to assume that oxygen is more soluble in the oil at higher temperatures, as a study of Fig. 8 shows that this rise is greater and occurs sooner at 50° than at 40°. Thus it would seem that this does indicate the presence of small amounts of readily oxidisable substances.

The proportion by which the inhibitors reduce the rate of oxidation is not affected much by temperature. Table II shows how much longer it takes the inhibited reaction, in the case of beta-napthol, to reach the indicated percentages as compared with the normal rate of oxidation of raw linseed oil.

TABLE II

The Proportional Increase in Time of the Inhibited Reaction over the Normal Reaction. Beta-naphthol is the Inhibitor.

Percentage of oxygen absorbed.	Increase at 40°	Increase at 50°	Increase at 100°
2.00	2.5	3.0	3.0
6.00	2.8	4.8	3.8
12.00	2.9	4.0	3.2
18.00	3.2	4.5	2.8

In Table III is indicated the ratio of oxygen absorbed in the inhibited reaction to the oxygen absorbed in the raw oil reaction at the times indicated in the left hand column.

TABLE III

Ratio of the Percentages of Oxygen absorbed in the Inhibited Reaction to that in the Normal Reaction, using Beta-naphthol.

Time, hrs. for 40° and 50° columns, min. for 100°.	Ratio at 40°	Ratio at 50°	Ratio at 100°
10	1.00	0.23	0.12
20	0.50	0.11	0.16
30	0.23	0.13	0.17
40	0.13	0.16	0.18
50	0.12	0.26	0.22

Thus it is seen that the inhibitor is slightly more effective at the lower temperature, and that it reduces the rate of oxidation more after six per cent of oxygen is absorbed than before.

Figs. 10, 11, and 12 show the result of using one per cent of diphenyl-amine as an inhibitor on the catalysed reaction, using 0.003 per cent of cobalt as the catalyst in the form of cobalt linoleate. This was done in the hope that some light might be cast on the "modus operandi" of inhibitors. The results show that an inhibitor does not act by suppression of catalyst alone. For if this were the case, from Fig. 10, curves 1 and 2 we must assume that one per cent of diphenyl-amine does not suppress all of the 0.003 per cent of cobalt. For the rate of reaction indicated by curve 2 is quite perceptibly greater than the linseed oil rate of oxidation. And so at 100° the same reaction, represented by Fig. 12, curve 2, would be expected to show a greater rate than that of Fig. 12, curve 3. It is, however, smaller than the rate of the raw oil reaction at this temperature. This points to the fact that the inhibitor and the catalyst exert their influence on the rate of reaction independently of each other even when present in the oil simultaneously.

Table IV shows the ratio of the time required for the inhibited reaction, using one per cent of diphenyl-amine as the inhibitor, to reach the percentages indicated in the left-hand column to the time required for the raw oil reaction to reach the same percentages. Both reactions are also catalysed with 0.003 per cent of cobalt.

TABLE IV

Ratio of the Time in the Reaction using Inhibitor and Catalyst to the Time in the Catalysed Reaction at the Indicated Corresponding Percentages.

Percentage of oxygen absorbed.	Ratio at 100°	Ratio at 50°
2.00	5.0	8.0
5.00	2.0	8.25
10.00	3.4	9.6
15.00	2.6	8.0
20.00	2.4	8.0
24.00	2.5	9.4

This accentuates the point made earlier in the discussion that inhibitors are slightly more efficient at lower temperatures. In this case the inhibitor is retarding the rate of reaction approximately three times as much at 50° as at 100°.

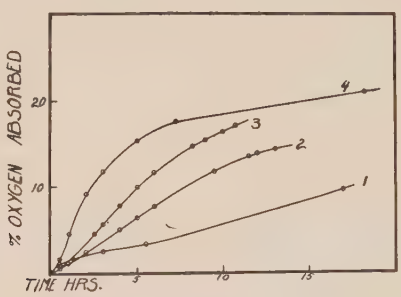

FIG. 13

Effect of Light on Oxidation of Linseed Oil.
Curve 1 Glass Vessel 30 cm. from lamp.
Curve 2 Quartz vessel 60 cm. from lamp.
Curve 3 Quartz vessel 30 cm. from lamp
Curve 4 Quartz vessel 15 cm. from lamp.

Fig. 13 represents the reaction in the presence of light. An Hanovia quartz mercury arc lamp was used as the source of light. Curve 1 shows the rate of oxidation of raw linseed oil in a soft glass vessel. Curves 2, 3, and 4 represent the results in a fused quartz apparatus. The following Table V shows the conditions of the experiments.

TABLE V

Light Intensity Data

Curve no.	Voltage of lamp.	Amperage.	Distance from lamp.	Temperature
1	40	2.4	30 cm.	20°.5
2	47	2.4	60 cm.	21°.0
3	40	2.4	30 cm.	20°.5
4	46	2.3	15 cm.	27°.0

All of the reaction can be ascribed to the action of light, for at these temperatures the dark reaction does not start during the time used for these observations. The curves show the rate of oxidation is not directly proportional to the intensity of the light falling on the system. The distance from the lamp in curve 4 is one half of that of curve 3, which in turn is one half of that of curve 2. The rate of curve 4 is roughly double that of curve 3, and the increase of curve 3 is only one half the rate of curve 2. The intensity varies inversely as the square of the distance from the lamp, consequently direct proportionality would call for a quadruple increase from curve 2 to 3, and the same from curve 3 to 4. In as much as curve 1 represents the reaction in a glass vessel, which cuts out most of the ultra-violet light, this curve represents the effect of visible light of this intensity on the reaction. The increase in rate of curve 3 over that of curve 1 shows the effect due to ultra-violet light alone.

Mr. H. L. J. Bäckström, of this laboratory, has obtained evidence that those reactions which are capable of being inhibited also give photo-chemical reactions in which more than one molecule of reacting substance undergoes combination per quantum of light energy. Thus, it was of interest to determine if this reaction did the same. The formula,

$$\frac{\text{Volts} \times \text{Amperes} \times 10^{7} \times A/4r^{2}}{5 \times 5 \times 6 \times 10^{-12}}$$

gives the number of quanta which are available in promoting the reaction, falling on a given area, A, of reacting space per second. The following assumptions are made in this formula. (1) One fifth of the electrical energy is given out as light energy. (2) None of the light falling on the system is reflected. (3) One fifth of the light energy is in the chemically active region. Table VI shows the number of oxygen molecules reacting per quantum of light energy in the four reactions, up to ten per cent of oxygen absorbed.

TABLE VI

Minimum Ratio of Molecules reacting per Quantum of Light Energy absorbed

Curve	Number of quanta per second	Number of molecules per second	Number of molecules per quantum	Distance from lamp
1	1.7×10^{16}	0.19×10^{16}	0.10	30 cm.
2	0.5×10^{16}	0.67×10^{16}	1.30	60 cm.
3	1.7×10^{16}	1.05×10^{16}	0.06	30 cm.
4	75.0×10^{16}	2.27×10^{16}	0.03	15 cm.

It must be emphasized that from the assumptions made in calculating the number of quanta, the number so obtained is a maximum value, consequently the number of molecules reacting per quantum are minimum values. The number actually reacting is probably greater than this. It will be noted that the further away the light source, the greater the yield per quantum. Taken in conjunction with the recorded deviation from the inverse square law, which will hold more precisely the greater the distance, it may be concluded that a chain reaction will reveal itself definitely under improved experimental con-

ditions. That the length of the chains is small is indicated by the low efficiency of inhibitors as compared with their effect in other reactions, notably the benzaldehyde oxidation.

We have pointed out that Genthe showed how little the oxygen pressure affected the rate of oxidation. A study of our curves supports this view. When the manometer read 100 mm. the oxygen in the vessel was replenished. This point on the curves will vary with the particular size of apparatus used but is about 14.00 per cent in most cases. We have raised the oxygen pressure from 50 mm. to 150 mm. at this point, a three-fold increase in pressure, yet the points on either side of this show no discontinuity in the curve. This leads to an interesting conclusion. It shows that this method eliminates any difficulties from a film of oxidized linseed oil forming over the unoxidized oil. For, were this the case the rate of oxygen absorption would be governed by the rate of diffusion of oxygen through a film. That this is not the case is evidence that we are measuring the true rate of oxidation of the oil.

Summary

(1). A simple and convenient apparatus has been described for studying the rate of oxidation of non-volatile oils. This apparatus gives true oxidation values.

(2). When the concentration of a drier in linseed oil is increased, there is a certain concentration of drier at any one temperature beyond which further increase produces no effect on the rate of oxidation. This value is reached with 0.0003 per cent of cobalt in the form of cobalt linoleate at 100°.

(3). As the temperature is raised the effect of driers is less pronounced.

(4). The effect of three inhibitors, hydroquinone, beta-naphthol, and diphenyl-amine, on the rate of oxidation of linseed oil has been studied. In general, the inhibitor is more effective at lower temperatures, and must be soluble in the oil to lend itself to quantitative study.

(5). Indication that the inhibitor does not act solely by suppression of a catalyst has been given, and that both inhibitor and catalyst may exert their influence independently.

(6). The effect of visible and ultra-violet light on the rate of oxidation of linseed oil at room temperature has been shown, using light of different and known intensities. The rate of reaction is not directly proportional to the intensity of the light as deduced from measurements made close to the light source. The reaction is very probably a chain reaction.

This work was carried out at the suggestion and under the direction of Professor Hugh S. Taylor, to whom I wish, here, to express my indebtness.